

N74-10274

paper No. 50

## THE FAR ULTRAVIOLET PHOTOLYSIS OF POLYMETHYLPHENYLSILOXANE FILMS ON QUARTZ SUBSTRATES

P. D. Fleischauer and L. Tolentino, *The Aerospace Corporation, El Segundo, California*

### ABSTRACT

Siloxane films containing phenyl and methyl substituents in different proportions were irradiated with ultraviolet light in the wavelength region 147-229 nm. This far ultraviolet irradiation produced increased equivalent solar absorptance  $\alpha_s$  of the films. The measured increases depend on the thicknesses and the composition of the films and on the wavelength of incident radiation.

### INTRODUCTION

The optical properties of second surface mirrors and other critical surfaces on spacecraft can be degraded significantly as a result of the formation of thin contaminant films on the surfaces. Mechanisms of contamination include improper cleaning before launch, condensation of volatile materials from other locations, and migration of adhesives and other materials near the critical surfaces. A critical aspect of thin film contamination is the susceptibility of the contaminants to damage by solar radiation and, in particular, by far ultraviolet (FUV) radiation. In space vacuum, this radiation can cause chemical reactions that change an initially transparent film into a partially absorbing one. This degradation, increase in  $\alpha_s$  of the mirror contaminant system, will depend on the amount of solar UV that is absorbed by the film (i.e., on the film thickness and on the wavelength dependent absorption coefficient), the chemical composition of the film, and possibly the temperature of the film during the irradiation.

The chemical composition and thickness of contaminant films on various critical surfaces depend on the sources of the contaminants and the proximity of the sources to the important surfaces. Silicone materials are used extensively in adhesives (e.g., RTV-566, 615) and in binders for paints (S 13 G); they constitute a major source of potential contaminants. We have chosen three different siloxane polymers that are probable contaminants from these sources and have investigated their optical properties as a function of FUV irradiation.

In this paper, we report on the FUV-induced changes in  $\alpha_s$  of contaminant films as a function of siloxane composition, film thickness, temperature, and wavelength of exciting radiation. The results show that the FUV induces near UV and visible absorption in the films. This induced absorption, increased  $\alpha_s$ , reaches a saturation value that increases with increases in film thickness and in the ratio of phenyl to methyl substituents in the siloxane. The amount of induced absorption is independent of the sample temperature during irradiation. Excitation wavelengths longer than  $\sim 230$  nm are quite ineffective in causing changes in  $\alpha_s$  for these films.

One of the original objectives of this study was to determine the thicknesses of contaminant films on optical surfaces that can be tolerated for various space missions. It may be concluded from our results that the answer to this question depends dramatically on the composition of the contaminant (i.e., whether or not it contains phenyl substituents). For example, a 1000 Å thick film of polydiphenylmethylsiloxane<sup>1</sup> would exhibit a saturation increase in  $\alpha_s$  of  $\sim 0.015$  after only  $\sim 500$  hr of solar UV irradiation, whereas a similar treatment of a 1000 Å film of polymethylsiloxane would result in a  $\Delta\alpha_s$  of only  $\sim 0.002$  at saturation.

## EXPERIMENTAL

### Deposition of Contaminants

Thin films of siloxane contaminants on quartz substrates (Industrial grade 7940) were prepared by first dissolving the siloxane in an appropriate solvent, usually xylene, and then applying a known volume of the solution to the substrate with a micropipet. After evaporation of the solvent, film thicknesses were determined ellipsometrically.<sup>2</sup> The films form with a small ring around the edge of the substrate and a uniform region in the center portion where all measurements are made. Typically, the ellipsometer results gave thicknesses from one-half to two-thirds of the values estimated from the solution concentration and volume and the substrate surface area.

### Irradiation Facility

The facility used for the irradiation of thin films and blank quartz slides consists of an all glass and metal, low-temperature Dewar, vacuum chamber for simultaneously maintaining two samples at a vacuum of  $\leq 10^{-6}$  Torr and at temperatures from  $-196^\circ\text{C}$  to above room temperature. The vacuum is maintained by pumping through a molecular sieve trap cooled to  $-196^\circ\text{C}$ , and there are no O ring or other type seals that could produce any outgassing within the vacuum chamber. An  $\text{Al}_2\text{O}_3$  window in the chamber permits irradiation of samples with 147, 163.3, 184.9, and 229 nm radiation. Calibration of these various lamps showed

the photon flux incident on the samples to be between  $10^{14}$  and  $10^{15}$  photons  $\text{cm}^{-2}\text{sec}^{-1}$ . The entire sample chamber can be removed from the vacuum system, while both temperature and vacuum conditions are maintained, for the measurement of transmission spectra of both the sample and the blank in the wavelength region of 200-800 nm with a Cary Model 15 Spectrophotometer. Irradiations of blank samples demonstrated that the chamber is contaminant free.

## RESULTS

Changes in solar absorptance  $\Delta\alpha_s$  were determined relative to blanks that had no films by measuring the visible-UV transmission spectrum before and after irradiation and then using a computer calculation to correlate these changes to the  $\alpha_s$  of second surface mirrors.<sup>3</sup> Two methods were used to correct the measured absorbance change in the sample for color center formation in the quartz substrates. The first involved estimating the fraction of the exciting (184.9 nm) light that is absorbed by the film, subtracting this fraction from the incident light flux to determine the change due to the quartz, and then correcting the total absorbance change for that due to quartz color center formation. The estimation of this "inner filter" effect was done by reference to the extent of formation of the 650 nm color center in the sample and blank quartz.<sup>3</sup> The contaminants did not absorb any light at 650 nm either before or after irradiation.

The second method involved warming the sample and blank to room temperature after irradiation at  $-100^\circ\text{C}$  and then remeasuring the transmission spectra. This annealing process bleached the quartz absorptions such that the contaminant FUV-induced absorption could be determined by simple subtraction of the blank (reflectance loss) from the sample. Both procedures agreed to within 10% of the  $\alpha_s$  determination, indicating that the warming step had little or no effect on the contaminant absorption.

The results of these irradiation experiments are shown in Figures 1-3. Figure 1 shows the FUV-induced absorption spectrum of a 2000 Å thick film of polydiphenylmethylsiloxane after different times of irradiation. As was the case for all of the irradiations, the sample was maintained in a clean vacuum chamber at pressures of  $\leq 10^{-6}$  Torr for both irradiation and spectral measurements. In this experiment, the temperature of the sample was controlled at  $-100^\circ\text{C}$  during the irradiations.

The initial spectrum shows a very small amount of absorption of the near UV and visible wavelengths, the spectral region that is important for the second surface mirrors. The FUV-induced absorption is composed of a tail from a FUV peak that extends out into the visible with a shoulder at  $\sim 260$  nm. As shown in Figures 1 and 2, this induced absorption increases rapidly during the first few hours of irradiation, but then the rate of increase

slows until a saturation value of  $\alpha_s$  is obtained. The magnitude of  $\Delta\alpha_s$  at saturation is very nearly proportional to the thickness of the contaminant film.

Figure 3 shows that the changes in  $\alpha_s$  also depend on the composition of the irradiated contaminant. For example, the material with a 4:1 ratio of phenyl to methyl groups on the siloxane backbone has a larger  $\alpha_s$  at saturation than the 2:1 material, which is, in turn, larger than the polymethylsiloxane (no phenyl groups). The differences between the first two, phenyl containing, materials are due to the extension of the induced absorption in the 4:1 material farther into the visible spectrum, even though the UV absorption at  $\sim 260$  nm is not quite as intense as for the 2:1 siloxane.

In the case of the polymethyl material, the decreased  $\Delta\alpha_s$  appears to be due to a decrease in the total amount of degradation and not just to a slower rate of approach to saturation. Unfortunately, for this material only one of the laboratory irradiation sources corresponds, in wavelength, to a feature in the initial absorption spectrum. For the phenyl containing materials, the simulation wavelengths are in the region of absorption maxima, whereas for the polymethyl material, only the 147 nm source was absorbed to a large extent by the contaminant film.

The temperature of the sample (contaminant) during irradiation has little effect on the changes in  $\alpha_s$ . Films of 2:1 phenyl to methyl material were irradiated at  $-100^\circ$  and  $25^\circ\text{C}$  for equivalent times. The results are included in Figure 3. Since no temperature effect was observed, many of the reported experiments were conducted at room temperature for convenience and in order to eliminate complications due to quartz substrate color center formation.

## DISCUSSION AND CONCLUSIONS

From the results of these irradiation experiments it is apparent that the combination of thin siloxane contaminant films on critical optical surfaces, such as second surface mirrors, and FUV solar irradiation can cause severe degradation of the optical properties of the mirrors. This degradation is made manifest by an increase in the solar absorption constant  $\alpha_s$  of the contaminant/mirror system. It is particularly critical if the contaminant contains phenyl substituents on the siloxane chain.

A film of a given thickness will reach a limiting or saturation value of  $\alpha_s$  that will be a function of the film thickness, its composition, and the wavelength of the exciting radiation. The saturation  $\alpha_s$  will not depend on the temperature of the contaminant during the exposure to the damaging radiation. Films that are  $\sim 500\text{\AA}$  thick can cause significant problems; they can have saturation  $\alpha_s$  values of  $\sim 0.005$ . However, the real difficulty would

be encountered if contaminants were continuously deposited on the mirror surface during a mission. Such continuous deposition must be limited such that film thicknesses do not exceed the critical values described in Figures 2 and 3.

It is also apparent from these results that normal solar simulation experiments that utilize high-pressure xenon lamps would not produce the degradation produced by these shorter wavelengths. Specifically, when a 2000 Å film of polydiphenylmethylsiloxane was irradiated with radiation at 229 nm, no measurable effect on  $\alpha_s$  was observed (Figure 2). The reasons for this large decrease in effect are: (1) the contaminant does not absorb a significant amount of 230 nm radiation and (2) the quantum yield for degradation is apparently much less for the lower energy radiation.

In certain space applications, such as in RTV adhesives, silicones that contain a high percentage of phenyl substitution have been used to provide certain desirable properties such as increased flexibility at low temperatures, increased resistance to particulate radiation, and potentially lower outgassing rates. The results of our experiments demonstrate that the effects of FUV solar radiation on the solar absorptance of potential contaminants must also be considered in choosing the proper materials for specific objectives. A film of polymethylsiloxane exhibits a factor of 5 times less  $\alpha_s$  degradation than an equivalent thickness of 4:1 phenyl to methyl siloxane. An alternative view is that for a given tolerable degradation in  $\alpha_s$ , a polymethylsiloxane film five times the thickness of a phenylmethyl film can be accommodated. Therefore, the advantages derived from phenyl substitution must exceed the factor of 5 loss in FUV radiation stability.

Finally, it must be recognized that these results represent the degradation of relatively pure samples of potential contaminants on critical spacecraft surfaces. Although impurity analyses were not performed, these candidate materials are almost certainly "cleaner" than actual contaminants. Consequently, the degradation reported, the changes in  $\alpha_s$ , represents "best possible" conditions in terms of the simulation of flight experience.

## REFERENCES

1. We refer to diphenylmethylsiloxane and tetraphenylmethylsiloxane. These materials are siloxanes with monomer units containing phenyl and methyl substituents in 2:1 and 4:1 ratios, respectively.
2. L. M. Dormant, to be presented at 7th AIAA-NASA/ASTM/IES Space Simulation Conference, Los Angeles, 12-14 November 1973.

3. H. K. A. Kan and L. H. Rachal, "Radiation-Induced Coloration in High-Purity Silica," to be published.

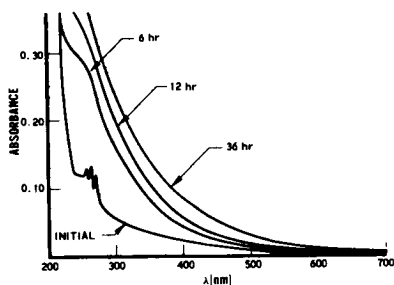


Fig. 1-Spectral changes for 184.9 nm irradiation of 2000 Å film of polydiphenylmethylsiloxane

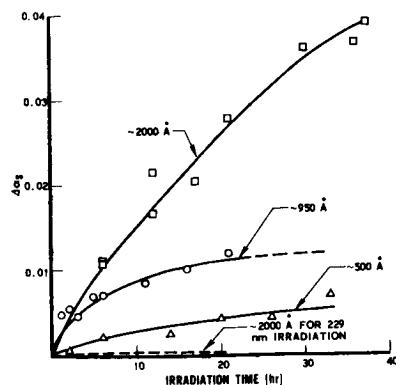


Fig. 2-FUV induced changes in  $\alpha_s$  of polydiphenylmethylsiloxane films at different thicknesses. 184.9 nm irradiation

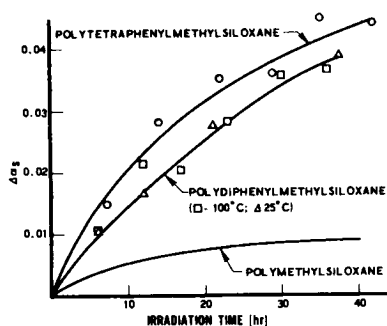


Fig. 3-FUV induced changes in  $\alpha_s$  of different siloxane films. 184.9 nm irradiation; all samples 2000 Å thick